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Imaging of highly oriented pyrolytic graphite corrosion accelerated by Pt particles

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Abstract

Carbon corrosion that is presumed to occur at the proton exchange membrane fuel cell (PEMFC) cathode was visualized by atomic force microscopy (AFM) and field emission-scanning electron microscopy (FE-SEM) observations using a fundamental model electrode. Platinum nanoparticles were deposited on a highly oriented pyrolytic graphite (HOPG) substrate as a model cathode catalyst, and its stability in an acid solution at a fixed potential was investigated. The formation of blisters on the surface of the model electrode was observed by AFM after it was kept at 1.0 V vs. RHE, especially at and around the Pt particles. FE-SEM observations using a backscattered electron detector revealed that Pt particles remained unchanged at their original positions after the formation of blisters.

Keywords: PEMFC; Degradation; HOPG; Electrochemical oxidation; AFM

1. Introduction

Over the past few years, extensive research on the proton exchange membrane fuel cell (PEMFC) has improved its performance [1], and it has just begun to be applied practically in electric vehicles and domestic cogeneration systems. However, before its commercialization, the production cost should be reduced, and its short operational life should be overcome. One of the main causes of long-term degradation is the decrease in cathode performance, which includes a decrease in the electrochemically active surface area of the catalyst and a decrease in the gas permeability of the gas diffusion layer. The latter may be due to an increase in hydrophilicity following electrochemical corrosion of the carbon surface. The former is due to an increase in particle size caused by aggregation and/or an Ostwald ripening mechanism, and probably also to the falling off of particles caused by carbon corrosion. Willsau and Heitbaum [2] reported the enhancement of CO_2 evolution from active carbon powder by a Pt catalyst using differential electrochemical mass spectroscopy (DEMS). They suggested that the Pt catalyst assists in the oxidation of the adsorbed CO species on the carbon surface. Roen et al. [3] detected CO_2 in a PEMFC cathode gas using on-line mass spectroscopy. They confirmed that CO_2 evolution from a Pt-catalyzed electrode was greater than that from a Pt-free electrode, which also indicated that Pt particles have some direct or indirect effects on carbon corrosion. This paper focuses on the changes in morphology on the surface of a Pt-deposited carbon substrate at a fixed potential in an acid solution, as a model electrode to elucidate the mechanisms of degradation. To achieve a high-resolution observation by atomic force microscopy (AFM), an HOPG plate was used for the carbon substrate. AFM [4,5] and scanning tunneling microscopy (STM) [6,7] observations of HOPG anodic oxidation induced by potential cycling have been reported. However, in these studies, no catalyst was used,

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and the oxidation potential was relatively high (upper limit of the potential cycling was not lower than 1.8 V vs. RHE) compared with the actual potential in the PEMFC cathode. In this study, the anodic oxidation of HOPG with Pt particles using fixed potentials at 1.0 and 0.9 V was examined.

2. Experimental

2.1. Electrodes

A freshly cleaved HOPG (NT-MDT Co.) basal plane was used for the substrate. Pt nanoparticles were deposited by pulse electrodeposition in an aqueous solution containing 1 mmol dm^{-3} H_2PtCl_6 and 2 mmol dm^{-3} HCl. A series of 20 potential pulses of −0.1 V vs. SHE for 0.1 s was used for the deposition. The Pt-deposited HOPG was then rinsed with deionized water.

2.2. Oxidation process

The Pt-deposited HOPG electrode was mounted in a cell with a reference electrode (Ag/AgCl) and a counter electrode (carbon paper). The electrolyte was a 1 mol dm^{-3} perchloric acid solution. The geometric area of the sample electrode was fixed at 0.442 cm^2 using an O-ring. The fixed potentials were 1.0 or 0.9 V vs. RHE for 70 h. After the oxidation process, the sample was again rinsed with deionized water.

2.3. Surface observation

AFM (Seiko Instruments, SPA300 unit + SPI3800 controller) observations were conducted in the oscillation mode (ca. 30 kHz) using a Si cantilever (2.5 N/m). The scanning speed was set at 2 μm s^{-1}. Field emission-scanning electron microscopy (FE-SEM) was also used for the observations. To distinguish the carbon morphology and its change from that of the Pt particles, both a secondary electron detector and a backscattered electron detector were used for imaging. AFM and SEM images obtained after oxidation were taken at the same position on the sample, which made it possible to discuss the changes in individual particles.

3. Results and discussion

Fig. 1(a) shows an AFM image of a Pt-deposited HOPG surface. Several tens of Pt particles with sizes of ca. 10 nm

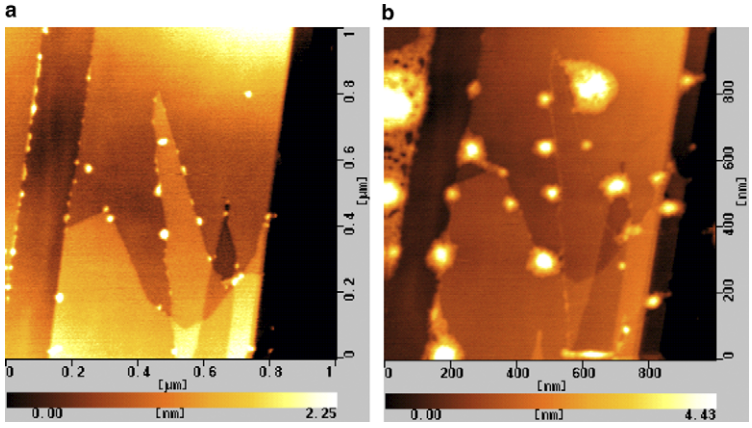

Fig. 1. AFM images (1 μm × 1 μm) of a Pt-catalyzed HOPG surface (a) before and (b) after potential retention at 1.0 V for 70 h in a 1.0 mol dm^{-3} $HClO_4$ solution.

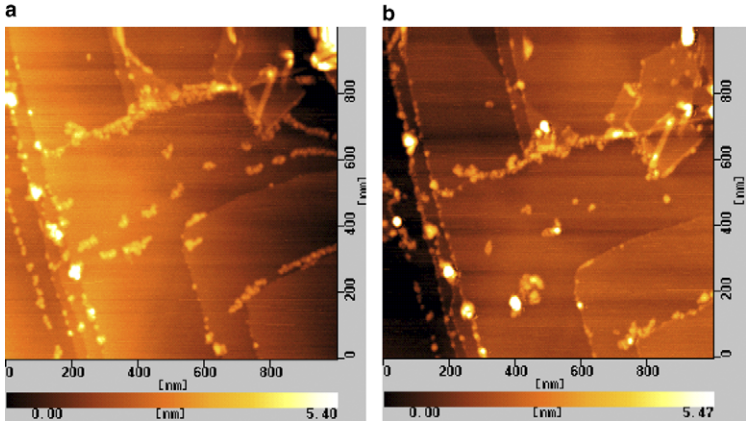

Fig. 2. AFM images (1 μm × 1 μm) of a Pt-catalyzed HOPG surface (a) before and (b) after potential retention at 0.9 V for 70 h in a 1.0 mol dm^{-3} $HClO_4$ solution.

were mainly deposited at the step edges of the graphite layers. After oxidation at 1.0 V for 70 h, Fig. 1(b) was obtained at the same position on the sample. A comparison of the features of the carbon steps in the two images confirms that the observation positions are identical. In Fig. 1(b), blisters are observed on the carbon surface. The blisters are ca. 5 nm high, and the lateral dimension reaches over 100 nm. Many of the blisters in Fig. 1(b) are located at the positions where Pt particles are located in Fig. 1(a), and it seems as if the Pt particles had grown. However, as mentioned later, the blisters are the structure of the carbon. The origin of the blisters is unclear at this stage. Goss et al. [4,5] reported dome-like blisters on a HOPG surface without platinum after potential cycling between ca. 0.3 and 1.8 V in a KNO_3 electrolyte, and assumed that the blisters are formed by gas evolution inside the graphite layer following carbon corrosion. However, this mechanism requires the prior intrusion of electrolyte inside the carbon layer. We considered that electrolyte enters by intercalation or infiltration from the grain boundary.

Fig. 2 shows the results for oxidation at 0.9 V. In contrast to the results at 1.0 V, the formation of blisters is not observed. Movement of the Pt particles can be observed, but there is no change in the original positions of the Pt particles. This seems to be due to the weak interaction between the Pt particles and the graphite basal plane. Although electrochemical oxidation of the graphite is thermodynamically possible above 0.2 V, there seems to be a critical potential between 0.9 and 1.0 V for blister formation under this experimental condition. Generally, among the carbon materials, graphitized carbon is more resistant to corrosion, and therefore it has been scarcely expected that HOPG would corrode at a potential as low as 1.0 V. In this study, the blisters were partly induced due to the effect of the Pt particles, and probably partly due to a lack of mechanical strength, since HOPG is easily exfoliated.

From Fig. 1(b), it cannot be confirmed whether or not Pt particles still exist after oxidation. Next, as shown in Fig. 3, SEM observations were performed during another experiment with oxidation at 1.0 V. After oxidation, the secondary electron detector, which tends to produce morphological imaging, shows blisters that cover the surface. On the other hand, Fig. 3(c), which was obtained using the backscattered electron detector, which tends to produce images of element differences, shows Pt particles clearly distinguished from the blisters. It is difficult to observe blisters in this figure because they are small and have a composition similar to that of the background. Each Pt particle seen in Fig. 3(c) is at its original position and there was no change in size compared with Fig. 3(a). Based on the results shown in Figs. 1 and 3, Pt particles are still present without falling off, despite carbon corrosion and subsequent blister formation. This is the first study to visualize HOPG corrosion at a site where Pt particles are located, and the results strongly suggest that Pt particles induce the formation of blisters around them. As mentioned above, blister formation may be partly due to characteristics of HOPG, so phenomena observed on HOPG in this work can not be directly regarded as that in real gas diffusion electrode of PEMFCs. However, based on the result that Pt catalyst accelerates CO_2 evolution from PEMFC [3], our observations should have significance to clarify the mechanisms of the acceleration by Pt particles.

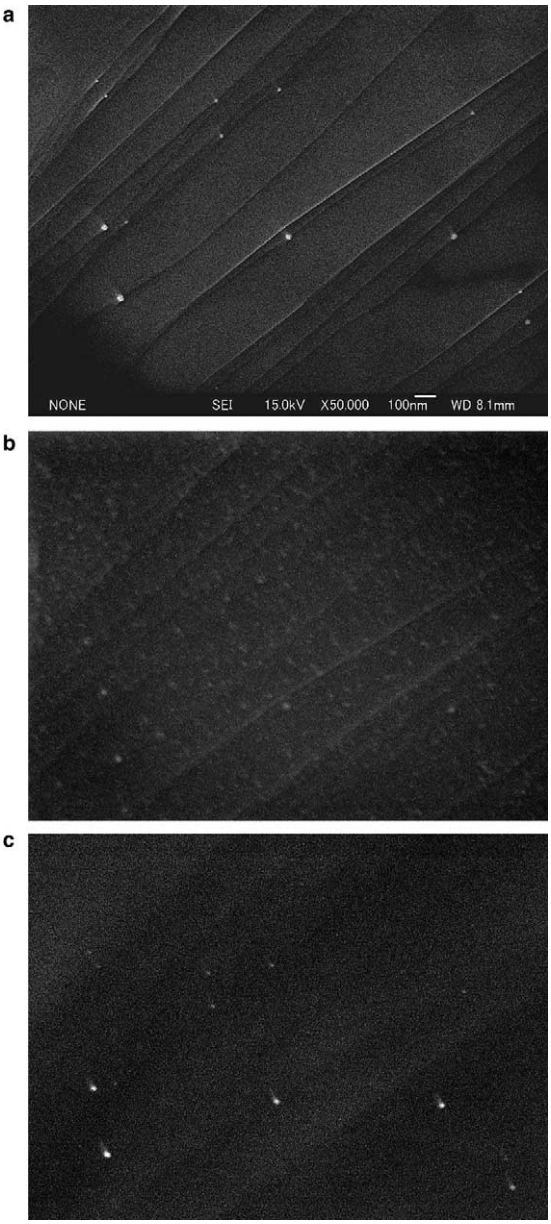

Fig. 3. SEM images (1.6×2 μm) of a Pt-catalyzed HOPG surface (a) before and (b), (c) after potential retention at 1.0 V for 70 h in a 1.0 mol dm^{-3} $HClO_4$ solution. A secondary electron detector was used for images (a) and (b), and a backscattered electron detector was used for image (c).

In addition, to investigate the stability of HOPG alone, AFM observations of the surface of freshly cleaved HOPG without Pt particles were made before and after potential retention at 1.0 and 1.2 V, respectively. At both 1.0 and 1.2 V, small blisters appeared on the surfaces. Thus, Pt particles promote, but are not necessary for, blister formation. This is also suggested by Figs. 1(b) and 3(b) where blisters

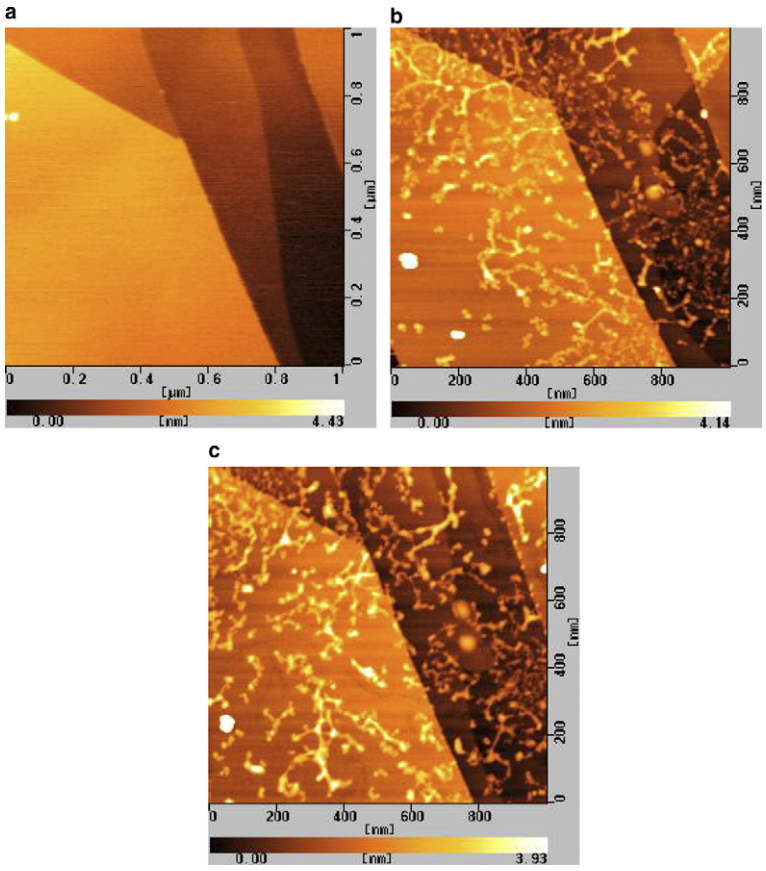

Fig. 4. AFM images (1 μm × 1 μm) of a Pt-catalyzed HOPG surface (a) before, (b) 70 h after and (c) 140 h after potential retention at 1.2 V in a 1.0 mol dm^{-3} $HClO_4$ solution.

are formed regardless of the presence of Pt particles. Fig. 4 shows the results of oxidation at 1.2 V for 70 h, followed by additional oxidation for 70 h at 1.2 V. Small blisters appeared after 70 h as mentioned above, and the number of blisters increased after the additional process. Based on these images, blister formation on the HOPG surface without Pt particles is slow and still in progress after 70 h. Systematic investigations on the effects of the potential and time on blister formation on HOPG with and without Pt particles are now underway.

4. Conclusions

Pt nanoparticles (ca. 10 nm) were electrodeposited on the surface of a HOPG substrate. Based on a comparison of AFM images before and after oxidation, blister formation was observed when the potential of oxidation was 1.0 V. On the other hand, oxidation at 0.9 V did not produce blisters. Based on FE-SEM observations using a backscattered electron detector, Pt particles were still observed after oxidation among blisters covering the surface, and at the same positions as before oxidation. At this point, blister formation is assumed to be caused by gas evolution following carbon corrosion. Many of the blisters were formed at and around Pt particles, which strongly suggests that the Pt particles contribute to blister formation. On the other hand, small blisters also appeared on a HOPG surface without Pt particles, which indicates that Pt is not necessary for blister formation.

Acknowledgments

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